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Conserving approximations in time-dependent density functional theory

Ulf von Barth,¹ Nils Erik Dahlen,² Robert van Leeuwen,² and Gianluca Stefanucci¹

¹*Solid State Theory, Institute of Physics, Lund University, Sölvegatan 14 A, S-22362 Lund, Sweden*

²*Rijksuniversiteit Groningen, Theoretical Chemistry, Materials Science Center, 9747AG, Nijenborgh 4, Groningen, The Netherlands*

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In the present work, we propose a theory for obtaining successively better approximations to the linear response functions of time-dependent density or current-density functional theory. The new technique is based on the variational approach to many-body perturbation theory (MBPT) as developed during the sixties and later expanded by us in the mid-nineties. Due to this feature, the resulting response functions obey a large number of conservation laws such as particle and momentum conservation and sum rules. The quality of the obtained results is governed by the physical processes built in through MBPT but also by the choice of variational expressions. We here present several conserving response functions of different sophistication to be used in the calculation of the optical response of solids and nanoscale systems.

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I. INTRODUCTION

Optical spectra constitute important tools for gaining information on the electronic structure of solids, molecules, and nanosystems. In many systems, the particle-hole interaction leads to a strong excitonic distortion of the optical spectrum—particularly in nanoscale objects. The theoretical description of such spectra is relatively sophisticated and very costly from a computational point of view. Some time ago, it was realized that these spectra are also within reach using time-dependent (TD) density-functional theory (DFT)—but with much less computational effort. From the Runge-Gross theorem¹ of TDDFT, we know how to construct the exact density response function of any electronic system in terms of an exchange-correlation kernel describing the particle-hole interactions. And from recent work by several researchers,^{2,3} we have a rather good idea about the properties of this kernel if it is to reproduce the rather accurate results obtained from solving the Bethe-Salpeter equation of many-body perturbation theory (MBPT). The kernel, usually named f_{xc} , has been calculated in the exchange-only approximation of TDDFT by several people in the past, see for instance Refs. 4 and 5. More recently, the kernel f_{xc} has been calculated in the same approximation by Petersilka, Gossmann, and Gross⁶ for the helium atom, by Kurth and von Barth for the density response of the homogeneous electron gas,⁷ and by Kim and Görling⁸ in the case of bulk silicon. In the cases of atomic helium and the homogeneous electron gas, the resulting response function represented a substantial improvement on that of the random phase approximation (RPA). The excitation energies of helium were much improved and the total energies obtained from the response function were much superior to those obtained from the RPA response function in both helium and the homogeneous electron gas. Unfortunately, this *ab initio* approach did not work very well in bulk silicon unless one rather arbitrarily introduces some kind of static screening of the particle-hole interaction.

In actual fact, within TDDFT, no systematic and realistic route toward successively better approximations has, so far, been available. In the present work, we have constructed

such a scheme based on the variational approach to many-body theory developed in Ref. 11. In terms of the one-electron Green's function of MBPT, these functionals give stationary expressions for the total action of the system at hand—or the total energy in the case of time-independent problems. From a stationary action, it is rather straightforward to construct the time-dependent density response function. Building the functionals from the Φ -derivable theory of Baym and Kadanoff,^{12,13} always results in response functions which obey essential physical constraints like particle, momentum, or energy conservation.

The simple idea of the present work is to restrict the variational freedom of the functionals to the domain of Green's functions which are noninteracting and given by a local one-electron potential—and vector potential, in the case of current DFT. According to the Runge-Gross theorem, this restriction immediately results in a density-functional theory, the quality of which is determined by the sophistication which is built in to the choice of the Φ -derivable approximation for the action functional. Thus, to every conserving scheme within MBPT, there is a corresponding level of approximation within TDDFT. The latter is determined variationally and there is no longer a need for an *ad hoc* procedure to equate corresponding quantities between TD-DFT and MBPT. A potentially interesting consequence of the theory proposed here, is that the often discussed linearized Sham-Schlüter equation¹⁴ for the exchange-correlation potential is nothing but the stationary condition for the action functional. In the particular version of the variational functionals developed in Ref. 11, and named Ψ -derivable theories, the screened Coulomb interaction also becomes an independent variable at one's disposal. This leads to approximations within TDDFT which are potentially as accurate as those of more elaborate schemes within MBPT, but which are comparatively easier to implement—especially in nanosystems and complex solids.

II. VARIATIONAL APPROACH TO TDDFT

Let us consider a system of interacting fermions exposed to an external, possibly time-dependent field $w(\mathbf{r}t)$. The full many-body Hamiltonian reads

$$\hat{H} = \hat{T} + \hat{U} + \hat{W}, \quad (1)$$

where

$$\hat{T} = -\frac{1}{2} \int d^3r \psi^\dagger(\mathbf{r}) \nabla^2 \psi(\mathbf{r})$$

is the kinetic operator, while

$$\hat{U} = \frac{1}{2} \int d^3r d^3r' \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}),$$

is the interaction operator [$v(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$]. The coupling to the external field is given by

$$\hat{W} = \int d^3r w(\mathbf{r}) \hat{n}(\mathbf{r}),$$

where $\hat{n}(\mathbf{r}) = \psi^\dagger(\mathbf{r}) \psi(\mathbf{r})$ is the density operator. The Green's function G obeys Dyson's equation

$$G = G_H + G_H \Sigma G,$$

where G_H is the Hartree Green's function and Σ is the exchange-correlation part of the electronic self-energy. Diagrammatic perturbation theory provides a tool for generating approximate self-energies and, in turn, approximate Green's functions. Except for physical intuition, the diagrammatic techniques rely solely on the validity of Wick's theorem.^{15,16} Thus, a typical contribution to the self-energy is represented by a diagram containing noninteracting propagators and interaction lines. However, any approximation which contains only a finite number of these diagrams violates many conservation laws. Conserving approximations require a proper choice of an infinite set of diagrams. The conserving approach by Baym¹² was based on such choices. Also the variational scheme by Almbladh, von Barth, and van Leeuwen¹¹ (ABL) was designed with the same objective in mind. The former approach is referred to as a Φ -derivable scheme because its central quantity is a universal functional, called Φ , of the one-electron Green's function G and the bare Coulomb potential v . It is constructed such that its functional derivative with respect to G gives the exchange-correlation part of the electronic self-energy Σ , whereas the functional derivative with respect to the Coulomb interaction v essentially gives the reducible polarizability χ of the system,

$$\Sigma(1,2) = \frac{\delta \Phi}{\delta G(2,1)}, \quad \chi(1,2) = -2 \frac{\delta \Phi}{\delta v(2,1)}. \quad (2)$$

[Here and in the following, we use the shorthand notation $1 = (\mathbf{r}_1, t_1)$, $2 = (\mathbf{r}_2, t_2)$ and so on.] Notice, however, that there is no reference to an actual system in the Φ functional. It acquires a meaning only when it is evaluated at a Green's function of an actual system. In the approach of ABL, the central quantity is instead the functional Ψ having the Green's function G and the screened Coulomb interaction W as independent variables. It is constructed so as to give the self-energy when it is differentiated with respect to G and the irreducible polarizability P when functionally differentiated with respect to W . Again, there is no reference to the actual system contained in the functional Ψ . By adding functional

pieces to the Φ or the Ψ functional, respectively, pieces which do contain clear connections to the system under study (like, e.g., the externally applied potential w), one constructs functionals for the total energy—or the action in the case of time-dependent problems—which, as functionals of G , have their stationary point at the Green's function G which is the solution to Dyson's equation. In the case of the Ψ -based functionals, they are also stationary when the screened interaction W obeys the so-called reduced Bethe-Salpeter equation to be discussed later.

The first variational functional of this kind was constructed by Luttinger and Ward¹⁷ (LW). It is a Φ functional and it has the appearance

$$iY_{\text{LW}}[G] = \Phi[G] - \text{Tr}\{\Sigma G + \ln(\Sigma - G_H^{-1})\} - iU_H[G]. \quad (3)$$

In Eq. (3), the functional $U_H[G] = -(i/2) \text{Tr}\{V_H G\}$ is the classical Hartree energy, $V_H(\mathbf{r}t) = \int d^3r' v(\mathbf{r}, \mathbf{r}') n(\mathbf{r}'t)$ is the Hartree potential, and $n(\mathbf{r}t)$ is the electron density. The symbol Tr (Trace) denotes a sum over labels of one-electron states plus an integration over time, or frequency for equilibrium problems in the ground state, a sum over discrete frequencies, or an integral over imaginary times for elevated temperatures, or an integral along the Keldysh contour^{16,18,19} in the case of nonequilibrium problems.²⁰ It is straightforward to realize that Y_{LW} is stationary when G obeys Dyson's equation with the self-energy of Eq. (2). At the stationary point, the Green's function is fully conserving.

At this point, we would like to draw attention to a very interesting fact, the ramifications of which have yet to be discovered. The variational schemes are by no means unique. By adding to Y_{LW} , any functional $F[D]$, where

$$D[G] = G(G_H^{-1} - \Sigma[G]) - 1, \quad (4)$$

obeying

$$F[D=0] = \left(\frac{\delta F}{\delta D} \right)_{D=0} = 0,$$

one obtains a new variational functional having the same stationary point and the same value at the stationary point. It might, however, be designed to give a second derivative which also vanishes at the stationary point—something that would be of utmost practical value. Such possibilities could open up a whole new field of research.

Choosing to add $F[D]$ to the LW functional, where

$$F[D] = \text{Tr}\{-D + \ln(D + 1)\} \quad (5)$$

obviously has the desired properties, leads to the functional

$$iY_K[G] = \Phi[G] - \text{Tr}\{GG_H^{-1} - 1 + \ln(-G^{-1})\} - iU_H[G].$$

This functional was first written down by Klein²¹ and could thus be called the Klein functional in order to distinguish it from the LW functional above. Unfortunately, this functional is less stable (large second derivative) at the stationary point as compared to the LW functional.^{22–25} Since the construction of response functions for TDDFT from the variational functionals involve evaluating them at noninteracting Kohn-Sham Green's functions, one might expect a less stable functional to give rise to inferior response functions. And this is

something which has to be thoroughly investigated. But it is clear that the Klein functional is much easier to evaluate and manipulate as compared to, e.g., the LW functional.

All the Φ functionals lead to a Dyson equation which has to be solved self-consistently for G . This is, in general, a very demanding task because of the complicated satellite structure inherent to any interacting Green's function. This severe complication is, however, circumvented by switching to TDDFT.

Our approximations within TDDFT are just special cases of the variational functionals in which we restrict the variational domain of the Green's function to be all Green's functions obtainable from a one-electron Schrödinger equation with a *local* multiplicative potential—or vector potential in the case of current DFT.

We remark that this restriction on the variational freedom renders all the variational functionals density functionals.^{1,20,26} Given a density, there is a local potential which in a noninteracting system produces that density. This potential produces the noninteracting Green's function, which we use to evaluate our functionals. Thus, the variational approach naturally generates different approximations within DFT for static problems and within TDDFT for time-dependent problems or for the response functions of stationary problems. As we shall see, the exchange-correlation quantities depend on the choice of the action functional so that to every approximate Baym functional Φ correspond different approximate exchange-correlation potentials and kernels.

Below, we discuss TDDFT and TD current-DFT (TD-CDF) approximations in the framework of the Klein functional and of the LW functional. We also generalize the theory to Ψ functionals and give some examples of approximations which we believe to be quite feasible to apply to realistic systems taking due account of the full electronic structure of one-body origin.

III. TDDFT FROM THE KLEIN FUNCTIONAL

Let G_s be the Green's function of a noninteracting system of electrons exposed to the external, possibly time-dependent, potential $V(\mathbf{r}t)$. The Klein functional evaluated at G_s can then be regarded as a functional of V

$$iY_K[V] = \Phi[G_s] - \text{Tr}\{G_s G_H^{-1} - 1 + \ln(-G_s^{-1})\} - iU_H[G_s].$$

We could now directly use the stationary property of the Klein functional with respect to variations in the unknown one-body potential V in order to obtain an equation for that potential. Because of the simplicity of a noninteracting Green's function, however, the functional Y_K can first be manipulated to acquire a physically appealing form. This can, most easily, be seen in the static case elaborated below. The following equations are still valid in the case of time-dependent problems and/or problems at elevated temperatures. This, however, requires some reinterpretations of standard DFT quantities like, e.g., T_s or U_H , which then become functionals on the Keldysh contour.²⁷ For noninteracting Green's functions, the logarithm of the inverse of G_s is just the sum of the occupied eigenvalues contained in G_s .¹⁷ And the trace of $G_s G_H^{-1} - 1$ is just the integral of the particle den-

sity multiplied by the potentials $V - w - V_H$. Expressing the eigenvalues of the one-electron Hamiltonian $-\nabla^2/2 + V$ as expectation values then leads to,

$$Y_K[V] = -i\Phi[G_s] + T_s[n] + \int w n + U_H. \quad (6)$$

Here, the quantity $T_s[n]$ is the well-known functional for the kinetic energy of noninteracting electrons in the potential V , which produces the density n . Comparing now with standard DFT, we see that the Φ functional precisely plays the role of the exchange-correlation energy. This means that we may reuse standard DFT results and realize that the Klein functional is stationary when

$$V = w + V_H - i \frac{\delta \Phi}{\delta n}, \quad (7)$$

where the last term is the exchange-correlation potential v_{xc} . Using the chain rule for differentiation, we can rewrite v_{xc} as

$$v_{xc} = -i \frac{\delta \Phi}{\delta n} = -i \int \frac{\delta \Phi}{\delta G_s} \frac{\delta G_s}{\delta V} \frac{\delta V}{\delta n}. \quad (8)$$

Remembering that the derivative of Φ with respect to the Green's function is just the self-energy Σ of our Φ -derivable theory and that the last factor is the inverse of the density response function χ_s of noninteracting electrons, we finally arrive at the equation

$$\int \Sigma_s(2,3) \Lambda(3,2;1) d(23) = \int \chi_s(1,2) v_{xc}(2) d2, \quad (9)$$

where we have defined a generalized noninteracting response function Λ according to

$$i\Lambda(2,3;1) \equiv \frac{\delta G_s(2,3)}{\delta V(1)} = G_s(2,1) G_s(1,3),$$

in terms of which we have $\chi_s(1,2) = \Lambda(1,1;2)$.

Equation (9) is exactly the “linearized” form of the Sham-Schlüter (SS) equation, i.e., it can be obtained from the SS equation¹⁴ by replacing the interacting G with G_s , and Σ with $\Sigma_s = \Sigma[G_s]$. Thus, the linearized SS equation follows from a variational principle. We realize that the variational approach can be used to obtain successively better approximations to the exchange-correlation potential v_{xc} by making successively better approximations to the functional Φ . In addition, the Φ -derivability and the variational property renders any approximation fully conserving.

The full density response function expressed in the manner of TDDFT is⁶

$$\chi = \chi_s + \chi_s(v + f_{xc})\chi, \quad f_{xc}(1,2) = \frac{\delta v_{xc}(1)}{\delta n(2)}.$$

The kernel f_{xc} can now be obtained from one further variation with respect to the total potential V . The variation of v_{xc} with respect to V can be expressed in terms of the exchange-correlation kernel f_{xc} as

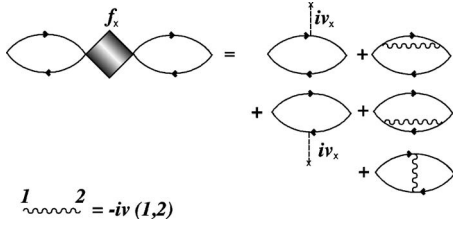


FIG. 1. Exchange-correlation kernel in the EXX approximation.

$$\frac{\delta v_{xc}(1)}{\delta V(2)} = \int f_{xc}(1,3)\chi_s(3,2)d3.$$

Thus, by varying Eq. (9), we obtain the following equation for f_{xc}

$$\begin{aligned} & \int \chi_s(1,3)f_{xc}(3,4)\chi_s(4,2)d(34) \\ &= \int \frac{\delta \Sigma_s(3,4)}{\delta V(2)} \Lambda(4,3;1)d(34) \\ &+ \int \Lambda(1,3;2)\Delta(3,4)G_s(4,1)d(34) \\ &+ \int G_s(1,3)\Delta(3,4)\Lambda(4,1;2)d(34), \end{aligned} \quad (10)$$

where

$$\Delta(1,2) = \Sigma_s(1,2) - \delta(1,2)v_{xc}(1).$$

When the potential v_{xc} has been obtained from Eq. (9), the right-hand side of Eq. (10) is a calculable expression for any given approximate Φ and no self-consistency is required. As an additional bonus, all occurring Green's functions are non-interacting as opposed to interacting as one would have in most iterative schemes based on MBPT. (Consider, e.g., the response function of the time-dependent Hartree-Fock approximation.)

A. The exchange-only approximation

Let us consider, for instance, the simplest approximation for Φ , namely the Hartree-Fock approximation

$$\Phi_x = \frac{i}{2} \text{Tr}\{GGv\}$$

from which we obtain

$$\Sigma_x(1,2) = \frac{\delta \Phi_x}{\delta G(2,1)} = iv(1,2)G_s(1,2).$$

In this case,

$$\frac{\delta \Sigma_x(1,2)}{\delta V(3)} = iv(1,2)G_s(1,3)G_s(3,2),$$

and Eq. (10) leads to the diagrammatic expansion in Fig. 1. This approximation is also known as the *exchange-only* (EXO) approximation or sometimes the *exact exchange*

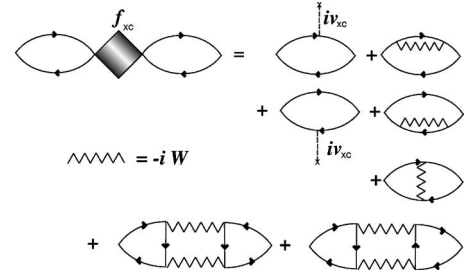


FIG. 2. Exchange-correlation kernel in the GW approximation.

(EXX) approximation. It has been evaluated earlier by several people.^{4–10}

B. The GW approximation within TDDFT

Let us now go one level higher in the expansion of many-body perturbation theory and include all the screening diagrams. This is called the GW level with Φ given by

$$\Phi[G_s] = \frac{1}{2} \text{Tr}\{\ln(1 + ivG_sG_s)\}.$$

The expression of the self-energy in the GW approximation becomes

$$\Sigma_s(1,2) = iG_s(1,2)W(1,2), \quad W = [1 - v\chi_s]^{-1}v.$$

To calculate the variational derivative of the self-energy with respect to V , we need to evaluate the change in the screened potential W . This can easily be constructed by observing that $W^{-1} = v^{-1} - \chi_s$ and that $\delta W / \delta V = -W[\delta W^{-1} / \delta V]W$. The final result is displayed in Fig. 2 in terms of Feynman diagrams.

All Green's functions are Kohn-Sham Green's functions and all interactions are RPA screened interactions. This response function for which the “time-dependent GW (TDGW) response” would be a descriptive name, is presently too difficult to compute in real systems. Geldart and Taylor used it to investigate the effects of the static screening properties on the electron gas.²⁸ It was used by Langreth and Perdew²⁹ in the static long wavelength limit in order to extract gradient approximations for DFT. Richardson and Ashcroft³⁰ have published an approximation to the TDGW response of the electron gas, but only at imaginary frequencies. Another application of the TDGW response is due to Langreth *et al.*³¹ and deals with Van der Waals forces. The TDGW response is generally believed to be very accurate but the computation of the screened interaction is known to be a bottle neck in GW calculations on real solids. Unfortunately, the TDGW response contains two such complicated factors (screened interactions).

C. TDCDFT from the Klein functional

In TDCDFT, the density n and the physical current density \mathbf{j} are uniquely fixed by the external vector potential \mathbf{A}_{ext} and the scalar potential w .^{32,33} The coupling to the external fields is given by

$$\hat{J} = \int d^3r [\mathbf{A}_{\text{ext}}(\mathbf{r}t) \cdot \mathbf{j}_p(\mathbf{r}t) + \tilde{w}(\mathbf{r}t)n(\mathbf{r}t)],$$

where $\tilde{w} = w + \mathbf{A}_{\text{ext}}^2/2$ and \mathbf{j}_p is the paramagnetic current operator. According to our prescription, we render the Klein functional a functional of $j_\mu = (n, \mathbf{j})$ by restricting the variational freedom of the Green's functions to be all those G'_s which are noninteracting and given by a local scalar potential and a vector potential, $A_\mu = (V, \mathbf{A})$. It is convenient to consider the four-vector $\tilde{A}_\mu = (\tilde{V}, \mathbf{A})$, where $\tilde{V} = V + \mathbf{A}^2/2$, as the independent variables since the four-vector density $j_{p,\mu} = (n, \mathbf{j}_p)$ is coupled linearly to \tilde{A}_μ .

As in the case of only density variations, the simplicity of a noninteracting Green's function again allows the Klein functional to be written in a much more convenient form. Using similar manipulations as in the beginning of Sec. III, we arrive at the expression

$$Y_K = T_s[n, \mathbf{j}] + U_H + \int \tilde{A}_\mu j_{p,\mu} - i\Phi, \quad (11)$$

where we have used the normal convention to sum over repeated indices. Here, the functional T_s for the noninteracting kinetic energy also depends on the physical current density \mathbf{j} and not only on the density n . As before, the Φ functional plays the role of the exchange-correlation energy. We then realize that the functional Y_K is stationary when

$$\tilde{V} = \tilde{w} + V_H + v_{xc}, \quad v_{xc} = -i \frac{\delta \Phi}{\delta n}, \quad (12)$$

$$\mathbf{A} = \mathbf{A}_{\text{ext}} + \mathbf{A}_{xc}, \quad \mathbf{A}_{xc} = -i \frac{\delta \Phi}{\delta \mathbf{j}}. \quad (13)$$

Let us now focus on those systems with a vanishing external vector potential. Following the same steps as led to Eq. (9), i.e., the chain rule for differentiation, we obtain the linearized Sham-Schlüter equation of TDCDFT,^{34,35}

$$\int \Sigma_s(2,3) \Lambda_\mu(3,2;1) d(23) = \int \chi_{s,\mu\nu}(1,2) A_{xc,\nu}(2) d2. \quad (14)$$

[Notice that $A_{xc,\mu} = (v_{xc}, \mathbf{A}_{xc})$ in normal four-vector notation.] The generalized response function Λ_μ appearing above is defined according to

$$i\Lambda_0(2,3;1) \equiv \frac{\delta G_s(2,3)}{\delta V(1)} = G_s(2,1)G_s(1,3), \quad (15)$$

$$i\Lambda(2,3;1) \equiv \frac{\delta G_s(2,3)}{\delta \mathbf{A}(1)} = \frac{1}{2i} G_s(2,1) [\tilde{\nabla}_1 - \tilde{\nabla}_1] G_s(1,3), \quad (16)$$

and from this response function, we obtain the Kohn-Sham density-density, current-density, and current-current response functions from the relation below

$$\chi_{s,\mu\nu}(1,2) = \frac{\delta j_\mu(1)}{\delta A_\nu(2)}. \quad (17)$$

The many-body response function

$$\chi_{\mu\nu}(1,2) = \frac{\delta j_\mu(1)}{\delta A_{\text{ext},\nu}(2)}, \quad A_{\text{ext},\nu} = (w, \mathbf{A}_{\text{ext}})$$

can be expressed in terms of the Kohn-Sham response function $\chi_{s,\mu\nu}$ through the exchange-correlation kernel $f_{xc,\mu\nu}$

$$\chi_{\mu\nu} = \chi_{s,\mu\nu} + \chi_{s,\mu\rho} (f_{xc,\rho\sigma} + \delta_{\rho\sigma} U) \chi_{\sigma\nu}, \quad (18)$$

where $f_{xc,\mu\nu} = \delta A_{xc,\mu} / \delta j_\nu$. In our variational scheme, the equation for f_{xc} is obtained from one further variation of Eq. (14) with respect to the Kohn-Sham potential A_μ . The corresponding response function $\chi_{\mu\nu}$ obeys the f -sum rule and Ward identities¹⁹ since under a gauge transformation the scalar potential V and vector potential \mathbf{A} change as in the exact CDFT, namely $V \rightarrow V + df/dt$ and $\mathbf{A} \rightarrow \mathbf{A} + \nabla f$. In order to prove this property, we change the external fields according to $w \rightarrow w + df/dt$, $\mathbf{A}_{\text{ext}} \rightarrow \mathbf{A}_{\text{ext}} + \nabla f$, and we ask the question how the scalar potential V and vector potential \mathbf{A} change at the stationary point. From Eqs. (12) and (13), it is straightforward to realize that $V \rightarrow V + df/dt$ and $\mathbf{A} \rightarrow \mathbf{A} + \nabla f$ provided the exchange-correlation potentials change according to $v_{xc} \rightarrow v_{xc} + \mathbf{A}_{xc} \cdot \nabla f$ and $\mathbf{A}_{xc} \rightarrow \mathbf{A}_{xc}$. Taking into account that under this gauge transformation $G_s(1,2) \rightarrow e^{-if(1)} G_s(1,2) e^{if(2)}$, it is a matter of very simple algebra to show that the linearized SS equation (14) is gauge invariant for any Φ -derivable self-energy.

D. The EXO within TDCDFT

Let us consider, for instance, the exchange-only approximation for the homogeneous electron gas. Extracting the time-ordered component of Eq. (18) and taking advantage of the translational invariance of the homogeneous electron gas, we find³⁴

$$\chi_{s,\mu\rho}(\mathbf{q}, \omega) f_{xc,\rho\sigma}(\mathbf{q}, \omega) \chi_{s,\sigma\nu}(\mathbf{q}, \omega) = V_{\mu\nu}(\mathbf{q}, \omega) + S_{\mu\nu}(\mathbf{q}, \omega),$$

where all quantities are time ordered and where $V_{\mu\nu}$ and $S_{\mu\nu}$, at zero temperature, are given by

$$V_{\mu\nu}(\mathbf{q}, \omega) = \int d^3p d^3k p_\mu v(|\mathbf{p} - \mathbf{k}|) k_\nu \times \left\{ \frac{\theta_{\mathbf{p}+\mathbf{q}/2} \bar{\theta}_{\mathbf{p}-\mathbf{q}/2}}{\omega - \varepsilon_{\mathbf{p}+\mathbf{q}/2} + \varepsilon_{\mathbf{p}-\mathbf{q}/2} - i\eta} - \frac{\bar{\theta}_{\mathbf{p}+\mathbf{q}/2} \theta_{\mathbf{p}-\mathbf{q}/2}}{\omega - \varepsilon_{\mathbf{p}+\mathbf{q}/2} + \varepsilon_{\mathbf{p}-\mathbf{q}/2} + i\eta} \right\} \times \left\{ \frac{\theta_{\mathbf{k}+\mathbf{q}/2} \bar{\theta}_{\mathbf{k}-\mathbf{q}/2}}{\omega - \varepsilon_{\mathbf{k}+\mathbf{q}/2} + \varepsilon_{\mathbf{k}-\mathbf{q}/2} - i\eta} - \frac{\bar{\theta}_{\mathbf{k}+\mathbf{q}/2} \theta_{\mathbf{k}-\mathbf{q}/2}}{\omega - \varepsilon_{\mathbf{k}+\mathbf{q}/2} + \varepsilon_{\mathbf{k}-\mathbf{q}/2} + i\eta} \right\}, \quad (19)$$

$$S_{\mu\nu}(\mathbf{q}, \omega) = \int d^3p p_\mu p_\nu \left\{ \frac{\bar{\theta}_{\mathbf{p}+\mathbf{q}/2} \theta_{\mathbf{p}-\mathbf{q}/2}}{(\omega - \varepsilon_{\mathbf{p}+\mathbf{q}/2} + \varepsilon_{\mathbf{p}-\mathbf{q}/2} + i\eta)^2} - \frac{\theta_{\mathbf{p}+\mathbf{q}/2} \bar{\theta}_{\mathbf{p}-\mathbf{q}/2}}{(\omega - \varepsilon_{\mathbf{p}+\mathbf{q}/2} + \varepsilon_{\mathbf{p}-\mathbf{q}/2} - i\eta)^2} \right\} \times \{\Sigma_x(\mathbf{p} + \mathbf{q}/2) - \Sigma_x(\mathbf{p} - \mathbf{q}/2)\}. \quad (20)$$

Here, we have denoted by p_μ, k_μ the four-dimensional vectors of components $(1, \mathbf{p})$, $(1, \mathbf{k})$, while the Heaviside step functions

$$\theta_q = \theta(\varepsilon_F - \varepsilon_q) \text{ and } \bar{\theta}_q = 1 - \theta_q$$

contain the Fermi energy ε_F .

In the large ω limit, the sum $V_{00} + S_{00}$ goes like $1/\omega^4$ and, therefore, $\chi_{00} = \chi_{s,00} + O(1/\omega^4)$. Since the residue of the second-order pole in $\chi_{s,00}$ only depends on the density, the approximated response function χ_{00} obeys the f -sum rule, as it should.

E. Conservation laws

As mentioned several times, the variational and Φ -derivable approach to TDDFT leads to density-functional approximations, which preserve many physical properties when the system is subject to external perturbations. Of course, TDDFT being a one-electron-like theory with a multiplicative potential trivially obeys the continuity equation and, thus, particle conservation for any approximation to exchange and correlation. The conservation of other quantities will, however, depend on the choice of such approximations.

In this section, we will, as an example, show how momentum conservation follows from the general formalism. In the one-electron-like theory of TDDFT, the change of total momentum per unit time is simply given by $\int n \nabla (w + V_H + v_{xc})$. The approximation to exchange and correlation is momentum conserving provided v_{xc} satisfies the zero force theorem.³⁶ Designing exchange-correlation potentials that fulfill such a constraint is nontrivial,³⁷ and several well-known approximations are actually not conserving.^{38,39} Below, we show that any approximate v_{xc} generated by our variational approach is fully conserving.

From Sec. III, we know that the change $\delta\Phi$ in the Φ functional is just

$$\delta\Phi = i \int v_{xc}(1) \delta n(1) d1 \quad (21)$$

when we change the one-body potential from V to $V + \delta V$. In the variational approach, *à la* Klein, Eq. (21) plays a similar role as the Baym construction $\delta\Phi = \text{Tr}[\Sigma \delta G]$. In order to prove the conservation of the total momentum, we have to show that v_{xc} does not exert any force on the Kohn-Sham system. Let us shift all coordinates by the same time-dependent infinitesimal vector $\delta(t)$. The functional Φ does not change since the interaction potential is invariant under translations. This implies that

$$0 = \delta\Phi = i \int v_{xc}(1) \delta(t_1) \cdot \nabla_1 n(1) d1. \quad (22)$$

One partial integration and the fact that the vector $\delta(t)$ is arbitrary and independent of position gives

$$\int n(\mathbf{r}t) \nabla v_{xc}(\mathbf{r}t) d^3r = 0. \quad (23)$$

This means that there is no contribution from exchange and correlation to the total force applied to the system which is given by the classical expression $\mathbf{F} = -\int n \nabla w$, as it should.

The proof of momentum conservation in the presence of vector potentials and currents follows in a similar way from the corresponding result

$$\delta\Phi = i \int A_{xc,\mu}(1) \delta j_\mu(1) d1, \quad (24)$$

which we obtained from the Klein functional.

IV. LW FUNCTIONAL

Let us now discuss the variational functional of Luttinger and Ward. From Eq. (3), we find

$$i\delta Y_{LW} = \text{Tr} \left\{ \left(\frac{1}{G_H^{-1} - \Sigma_s} - G_s \right) (\delta \Sigma_s + \delta V_H) \right\}.$$

We introduce the auxiliary Green's function \tilde{G} according to

$$\tilde{G} = \frac{1}{G_H^{-1} - \Sigma_s} = G_H + G_H \Sigma_s \tilde{G},$$

i.e., \tilde{G} represents the first iteration toward the full self-consistent many-body Green's function starting from the Kohn-Sham Green's function G_s . Writing the total potential V as

$$V = w + V_H + v_{xc}$$

and eliminating G_H between G_s and \tilde{G} , one obtains $\tilde{G} = G_s + \tilde{G}[\Sigma_s - v_{xc}]G_s$, and thus

$$i \frac{\delta Y_{LW}}{\delta V(1)} = \text{Tr} \left\{ \tilde{G}[\Sigma_s - v_{xc}] G_s \left[\frac{\delta \Sigma_s}{\delta V(1)} + \frac{\delta V_H}{\delta V(1)} \right] \right\}. \quad (25)$$

In the Hartree-Fock approximation, $\Sigma_s \simeq \Sigma_x$ and Eq. (25) yields

$$\begin{aligned} & \int \tilde{G}(2,3) \Sigma_x(3,4) G_s(4,5) v(2,5) \Lambda(5,2;1) d(2345) \\ &= \int \tilde{G}(2,3) v_{xc}(3) G_s(3,2) v(2,4) \chi_s(4,1) d(234). \end{aligned}$$

This equation determines the exchange-correlation potential which, in turn, fixes the total potential V and then G and \tilde{G} . We also observe that this v_{xc} is approximately linear in the strength of the Coulomb interaction as is the ordinary exchange potential v_x described in the context of the Klein functional. As in the case of the EXO approximation dis-

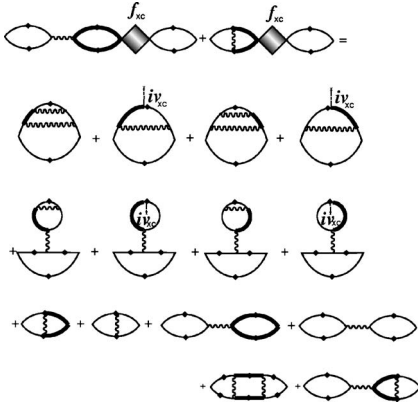


FIG. 3. Exchange-correlation kernel calculated from the LW variational approach to TDDFT in the Hartree-Fock approximation. The thin lines represent the noninteracting Green's function G_s , while the thick lines represent the Green's function \tilde{G} .

cussed above, the exchange-correlation part of the response function f_{xc} is obtained from one further variation with respect to the total potential V . The expression now becomes slightly more tedious but is still of the form $\hat{O}f_{xc} = g_{xc}$, where \hat{O} is a known operator and g_{xc} is a calculable expression which does not involve f_{xc} , see Fig. 3.

The response function of the LW functional at the Hartree-Fock level is expected to be superior to that of the EXO due to the better stability of the LW functional as compared to the Klein functional.

We also wish to emphasize that it made no difference to the resulting response function whether we used the LW functional or the Klein functional to derive it—provided we allowed free variations of the Green's function G . By restricting the possible choices of Green's functions to those produced by local potentials (TDDFT) the LW and Klein functionals give rise to different response functions at the same level of many-body perturbation theory.

V. Ψ FUNCTIONALS

The main advantage of the Ψ functionals is that they give the possibility of using physical models for the screening, the calculation of which is actually a bottleneck in practical applications. A word of caution is, however, appropriate in this context. With model screened interactions (W 's) there is usually no self-consistency with respect to W , a fact that might compromise the conserving property of the theory. The Ψ functionals have two independent arguments (G and W) resulting in terms linear in the deviation of the actual Green's function from the self-consistent one when W is away from the value which renders the functional stationary. When the Ψ functionals are used to construct response functions of TDDFT the theory is, however, variational with respect to the one-body potential generating the noninteracting Green's function—even when a model W is used. This fact actually restores several conserving properties although this has to be verified from case to case. For instance, choosing model W :s which, like the bare Coulomb interaction, is instantaneous

and translationally invariant will clearly not spoil the conserving properties.

The first Ψ functional was constructed by ABL in 1996.¹¹ It has the appearance

$$iY_{\text{ABL}}[G, W] = \Psi[G, W] - \text{Tr}\{\Sigma G - \ln(\Sigma - G_H^{-1})\} + \frac{1}{2}\text{Tr}\{WP + \ln(1 - vP)\} - iU_H[G]. \quad (26)$$

The ABL functional is stationary with respect to variations of G and W , whenever G obeys Dyson's equation and W obeys the “contracted Bethe-Salpeter equation,” $W = v + vPW$. As for the Φ functionals, the self-energy is obtained by taking the functional derivative of Ψ with respect to G and the polarization P turns out to be the negative of twice the functional derivative of Ψ with respect to W

$$\Sigma(1, 2) = \frac{\delta\Psi}{\delta G(2, 1)}, \quad P(1, 2) = -2 \frac{\delta\Psi}{\delta W(2, 1)}.$$

Just as was the case for the pure Φ functionals, we can add to any Ψ functional an arbitrary functional $K[Q]$ of a quantity Q defined by $Q = W(v^{-1} - P[G, W]) - 1$, with the properties

$$K[0] = \frac{\delta K}{\delta Q}[0] = 0.$$

We then obtain a new Ψ functional with the same stationary point and the same value at the stationary point. An example of a simple functional obtained in this way is

$$iY_{\text{LWS}}[G, W] = \Psi[G, W] - \text{Tr}\{\Sigma G - \ln(\Sigma - G_H^{-1})\} + \frac{1}{2}\text{Tr}\{Wv^{-1} - 1 + \ln(Wv^{-1})\} - iU_H[G].$$

Here, LWS stands for the simple version of the Ψ functional based on the construction of Luttinger and Ward. As for the Klein version of Φ -derivable functionals, we expect that this functional is less stable than the original ABL functional of Eq. (26). Also, it contains the same LW expression which led to the complicated result depicted in Fig. 3 and, for the moment, we deem this functional as less suitable for the construction of response functions.

Another possibility is to, instead, add to Y_{ABL} the functional $F[D]$ of Eq. (5), thus obtaining the Klein version of Ψ -derivable functionals

$$iY_{\text{ABLK}}[G, W] = \Psi[G, W] - \text{Tr}\{GG_H^{-1} - 1 + \ln(-G^{-1})\} + \frac{1}{2}\text{Tr}\{WP + \ln(1 - vP)\} - iU_H[G].$$

Again, due to the simplicity of the “Klein” expression, we can here use the same manipulations as we applied to the original Klein functional in order to arrive at Eq. (6). Thus, inserting the noninteracting Green's function G_s into the functional Y_{ABLK} , we then obtain

$$Y_{\text{ABLK}}[V] = T_s[n] + \int wn + U_H + E_{xc}[n], \quad (27)$$

where

$$E_{xc}[n] = -i\Psi[G_s, W] - \frac{i}{2}\text{Tr}\{WP[G_s, W] + \ln(1 - vP[G_s, W])\}.$$

Consequently, also this functional can be given the standard DFT form, and we realize that it is stationary at the noninteracting Green's function G_s produced by the local one-electron potential

$$V = w + V_H + \frac{\delta E_{xc}}{\delta n}. \quad (28)$$

In fact, all functionals, be they of the Φ or the Ψ variety, having the Klein form for their dependence on the external potential w have the nice property that the optimizing potential consists of the external potential w , the Hartree potential V_H , and the functional derivative of the exchange-correlation energy with respect to the density n . In Eq. (28), the last derivative is calculated from the chain rule for differentiation giving the optimized potential method (OPM) like equation

$$\begin{aligned} \int \chi_s(1,2)v_{xc}(2)d2 &= \frac{\delta E_{xc}}{\delta V(1)} \\ &= \int \Lambda(3,2;1) \left[\Sigma(2,3) \right. \\ &\quad \left. + \frac{1}{2} \int \Delta W(4,5) \frac{\delta P(5,4)}{\delta G_s(3,2)} d(45) \right] d(23). \end{aligned}$$

The quantity ΔW is $W - \tilde{W} = W - v/(1 - vP)$, and remember that we are here allowed to use any model for W . In particular, we could choose W to be \tilde{W} , in which case our equation for the exchange-correlation potential v_{xc} reduces to the same expression as obtained from the “Klein version” of the Φ formalism described in Sec. III. Furthermore, it is easily seen directly from its definition that the functional Y_{ABLK} becomes independent of the choice of model W at the level of the RPA. Thus, at that level, this functional does not add anything to the previously discussed Φ -derivable scheme at the same level (RPA). Being, for the moment, content with that level, we will here not pursue the Y_{ABLK} any further.

Finally, by adding an appropriate choice for the functional $K[Q]$, as discussed above, to the functional Y_{ABLK} , we obtain the simplest functional Y_{KK} of those discussed in the present work. We have

$$\begin{aligned} iY_{KK} &= \Psi - \text{Tr}\{GG_H^{-1} - 1 + \ln(-G^{-1})\} \\ &\quad + \frac{1}{2}\text{Tr}\{Wv^{-1} - 1 + \ln(Wv^{-1})\} - iU_H[G]. \end{aligned}$$

As before, we restrict the variational freedom of the Green's functions to noninteracting ones (G_s) and differentiate Y_{KK} with respect to the total, as it turns out, Kohn-Sham potential V producing the noninteracting G_s . Notice that W is an independent variable and does not depend on G_s or V . Only G_s depends on V . We obtain

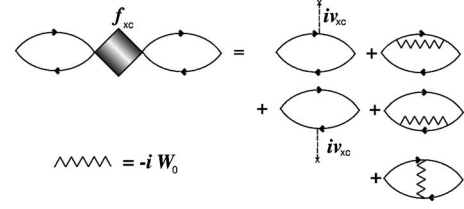


FIG. 4. Exchange-correlation kernel at the GW level in the Ψ scheme.

$$\int \Sigma_s(2,3)\Lambda(3,2;1)d(23) = \int \chi_s(1,2)v_{xc}(2)d2, \quad (29)$$

where $v_{xc} = V - w - V_H$, as before. We are now allowed to choose any appropriate but approximate $W = W_0$. Let us study the response function resulting from the functional Y_{KK} at the GW level, meaning that

$$\Psi = \frac{i}{2}\text{Tr}\{G_s G_s W_0\}.$$

Consequently, in this approximation, we obtain the GW_0 self-energy

$$\Sigma_s = \frac{\delta \Psi}{\delta G_s} = iG_s W_0.$$

One further variation of Eq. (29) with respect to V gives an equation for f_{xc} , whose diagrammatic representation is given in Fig. 4. Here, the Green's functions are Kohn-Sham Green's functions and the corresponding exchange-correlation potential is that which, to first order, reproduces the density of a GW calculation with some model W_0 . The screened interactions could be model interactions, e.g., Yukawa potentials, screened potentials within the RPA, or plasmon-pole approximations. The vertex diagram in Fig. 4 should be calculated with Kohn-Sham Green's functions. The sum of the first four self-energy diagrams is essentially, to first order, equivalent to a single polarization diagram calculated using GW_0 Green's functions.

If W_0 is chosen to be a Yukawa potential, i.e., a statically screened Coulomb interaction, this conserving GW_0 response function provides a justification of the work of Marini *et al.*³ provided the Green's function with GW (RPA) shifted poles is close to the Green's function of a Hartree-Fock calculation with a statically screened Coulomb potential.

The use of a Yukawa potential for a screened interaction also sheds some light on the work by Kim and Görling.⁸ They did exactly the TDDFT response function of Fig. 4 in bulk silicon using the bare Coulomb interaction for W . They found that their calculated optical absorption spectrum was far from an experimental result unless they, somewhat artificially, cut down the range of the particle-hole interaction.

It would actually be quite interesting to investigate the properties of the response function of Fig. 4 using a variety of screened interactions of the kind that preserves its conserving properties. An ongoing collaborative project^{40,41} has precisely this objective in mind.

VI. CONCLUSIONS AND OUTLOOKS

In the present work, we have proposed a new way of obtaining approximations to current and density response functions of realistic systems. Our theory is based on the variational approach to many-body theory as previously formulated by us and others. It gives the possibility to find successively better approximations to the effects of exchange and correlation in the framework of time-dependent density-functional or current density-functional theory. The fact that the theory is formulated in the language of TDDFT makes it much easier, from a computational perspective, to apply to realistic systems as compared to standard MBPT.

Improved approximations can be constructed in a systematic way in the same sense as within MBPT. But physical intuition as to what physical processes are important for any particular problem must be applied. The underlying variational approach to MBPT is not unique and many variational functionals can be constructed leading to the same quality of approximation. Our method for improved approximations within TDDFT has the same feature. Different functionals have different variational accuracy meaning different sizes of the second-order errors. In the present paper, we have discussed mainly two functionals—that due to Luttinger and Ward (LW) and that due to Klein (K). The former has proved to be more stable as compared to the latter as far as concerns the calculation of total energies of a variety of systems ranging from those with very localized electrons to those with itinerant electrons. This would suggest that the LW functional ought to be used also for the construction of response functions within TDDFT. In the present work, we have given the formulas for the exchange-correlation kernel of TDDFT resulting from both functionals. Sadly enough, we judge that of the supposedly better LW functional to be beyond our present computational facilities—even at a rather low level of approximation within MBPT. In order to demonstrate this point, we have given the diagrams representing the density response function resulting from the LW formulation within the exchange-only approximation. We would still like to draw attention to the fact that the ambiguity in the choice of functionals can most likely be used to our advantage. But much more research is needed in order to see how this should be done.

A very important feature of our variational approach to TDDFT is the fact it relies on the Φ or Ψ derivability of the underlying approximation within MBPT. Combined with the variational property of the chosen functional, this leads to the preservation of many physically important conservation laws and sum rules. And this is true regardless of the actual chosen level of approximation within MBPT. This highly desirable feature is not guaranteed in other available approaches based on straightforward diagrammatic expansions, iterative techniques, or decoupling schemes. For instance, in Ref. 42, one develops a diagrammatic representation for the particular many-body perturbation scheme which starts from a zeroth

order Hamiltonian which already gives the correct density.⁴³ Unfortunately, this technique suffers from the same basic drawbacks as ordinary MBPT—it is, in principle, divergent, summations must be carried to infinite order, and there is no guarantee for obtaining approximations which have certain desirable physical properties automatically included. The same holds true for expansions which are based on iterating the so-called Hedin equations⁴⁴ using the screened interaction as the “small” parameter.⁴⁵ As an example, we have, in the present work, demonstrated how the variational approach leads to momentum conservation in the case of the Klein functional.

It is worth observing that the so-called linearized Sham-Schlüter equation actually turns out to be a result of our variational approach starting from the Klein functional. But this is only true if the self-energy involved is a Φ -derivable or Ψ -derivable one. In that case, the resulting approximation for the response function is, of course, conserving.

We also remark that the so-called optimized potential method (OPM) and many generalizations thereof readily follows from the theory presented here. As an example, we have given the explicit formulas for the current-density response of a homogeneous system within the exchange-only approximation.

Even though we now have a systematic way of obtaining better response functions within TDDFT, the expressions quickly become too complicated to be implemented in low-symmetry systems, especially when we want to include all physically relevant processes. In this context, we advocate the use of the Ψ -derivable theories which allows for the use of model screened interactions without losing the important conserving properties. In this way, important physical effects like, e.g., a strong particle-hole interaction can be incorporated without an excessive increase in the computational effort. One should, however, keep in mind that models for the screened interaction must possess certain symmetries related to the actual system in order for the conserving properties to be preserved.

We have discussed the implementation of the theories presented here with other research groups. One particularly promising approach is that which is based on the Klein functional and the Ψ formulation using a model screened interaction like, e.g., a statically screened Coulomb interaction as often used in the Bethe-Salpeter approach, or a simple plasmon-pole approximation. Together with our collaborators,^{40,41} we hope to be able to present some numerical results within the near future.

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- ¹E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- ²L. Reining, V. Olevano, A. Rubio, and G. Onida, Phys. Rev. Lett. **88**, 066404 (2002).
- ³A. Marini, R. Del Sole, and A. Rubio, Phys. Rev. Lett. **91**, 256402 (2003).
- ⁴D. J. W. Geldart and R. Taylor, Can. J. Phys. **48**, 155 (1970).
- ⁵A. Holas, P. K. Aravind, and K. S. Singwi, Phys. Rev. B **20**, 4912 (1979).
- ⁶M. Petersilka, U. J. Gossmann, and E. K. U. Gross, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998), p. 177.
- ⁷S. Kurth and U. von Barth (unpublished).
- ⁸Y.-H. Kim and A. Görling, Phys. Rev. Lett. **89**, 096402 (2002).
- ⁹R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).
- ¹⁰J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
- ¹¹C.-O. Almbladh, U. von Barth, and R. van Leeuwen, Int. J. Mod. Phys. B **13**, 535 (1999).
- ¹²G. Baym, Phys. Rev. **127**, 1391 (1962).
- ¹³G. Baym and L. P. Kadanoff, Phys. Rev. **124**, 286 (1961).
- ¹⁴L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).
- ¹⁵A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover, New York, 2003).
- ¹⁶P. Danielewicz, Ann. Phys. (N.Y.) **152**, 239 (1984).
- ¹⁷L. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).
- ¹⁸L. V. Keldysh Zh. Eksp. Teor. Fiz. **47**, 1515 (1964); Sov. Phys. JETP **20**, 1018 (1965).
- ¹⁹R. van Leeuwen and N. E. Dahlen, in *The Electron Liquid Paradigm in Condensed Matter Physics*, Proceedings of the International School of Physics “Enrico Fermi,” Vol. 157, edited by G. F. Giuliani and G. Vignale (IOS Press, Amsterdam, 2004).
- ²⁰For functionals on the Keldysh contour, see also R. van Leeuwen, Phys. Rev. Lett. **80**, 1280 (1998).
- ²¹A. Klein, Phys. Rev. **121**, 950 (1961).
- ²²N. E. Dahlen and U. von Barth, Phys. Rev. B **69**, 195102 (2004).
- ²³N. E. Dahlen and U. von Barth, J. Chem. Phys. **120**, 6826 (2004).
- ²⁴N. E. Dahlen, R. van Leeuwen, and U. von Barth, Int. J. Quantum Chem. **101**, 512 (2005).
- ²⁵N. E. Dahlen, R. van Leeuwen, and U. von Barth Phys. Rev. A (to be published).
- ²⁶P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ²⁷For an elementary introduction to the Keldysh formalism, see R. van Leeuwen, N. E. Dahlen, G. Stefanucci, C.-O. Almbladh, and U. von Barth, *Introduction to the Keldysh Formalism and Applications to Time-Dependent Density Functional Theory*, Lecture Notes in Physics (Springer Verlag, Berlin, 2005); cond-mat/0506130.
- ²⁸D. J. W. Geldart and R. Taylor, Can. J. Phys. **48**, 167 (1970).
- ²⁹D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).
- ³⁰C. F. Richardson and N. W. Ashcroft, Phys. Rev. B **50**, 8170 (1994).
- ³¹D. C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard, and B. I. Lundqvist, Int. J. Quantum Chem. **101**, 599 (2005).
- ³²G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).
- ³³K. Capelle and G. Vignale, Phys. Rev. B **65**, 113106 (2002).
- ³⁴R. van Leeuwen, in *The Fundamentals of Electron Density, Density Matrix and Density Functional Theory in Atoms, Molecules and the Solid State*, edited by N. I. Gidopoulos and S. Wilson, Progress in Theoretical Chemistry and Physics Vol. 14 (Kluwer, Dordrecht, 2003).
- ³⁵R. van Leeuwen, in *Progress in Nonequilibrium Green's Functions II*, edited by M. Bonitz and D. Semkat (World Scientific, River Edge, NJ, 2003).
- ³⁶R. van Leeuwen, Int. J. Mod. Phys. B **15**, 1969 (2001).
- ³⁷J. F. Dobson, M. J. Bünner, and E. K. U. Gross, Phys. Rev. Lett. **79**, 1905 (1997).
- ³⁸J. B. Krieger, Yan Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).
- ³⁹R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
- ⁴⁰This is a collaboration between the San Sebastian and Lund nodes of the European Network of Excellence called NANO-QUANTA.
- ⁴¹A. Rubio and M. Grüning (private communication).
- ⁴²I. V. Tokatly and O. Pankratov, Phys. Rev. Lett. **86**, 2078 (2001).
- ⁴³A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).
- ⁴⁴L. Hedin, Phys. Rev. **139**, A796 (1965).
- ⁴⁵F. Bruneval, F. Sottile, V. Olevano, R. Del Sole, and L. Reining, Phys. Rev. Lett. **94**, 186402 (2005).